

## NITRIFICATION INHIBITOR TREATMENT OF GRAZED PASTURE SOILS

### Field of the Invention

This invention relates to a soil management tool when used in pasture farming systems to  
5 reduce nitrate leaching, reduce nitrous oxide emissions, reduce potassium, calcium and  
magnesium leaching, and improve pasture production from grazed pasture soils. More  
particularly it relates to a method for and the delivery of nitrification inhibitors (including  
dicyandiamide (DCD)) to treat grazed pasture soils to achieve the full range of benefits  
listed above.

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### Background Art

Nitrate ( $\text{NO}_3^-$ ) leaching from agricultural land and the contamination of ground- and  
surface-waters is a major environmental concern in many countries. This problem is  
particularly serious in intensive land use areas, where there are high inputs of nutrients in  
15 the forms of fertilizers or animal manure or effluents, or where nutrients are returned in the  
form of urine from grazing animals.

High  $\text{NO}_3^-$ -N leaching losses (over  $100 \text{ kg NO}_3^- \text{ N ha}^{-1} \text{ y}^{-1}$  when urea fertiliser was applied  
at  $200 \text{ kg N ha}^{-1} \text{ y}^{-1}$ ) have been reported on shallow stoney soils in Canterbury in the South  
20 Island of New Zealand. Studies in the UK on beef cattle grassland have recorded  $\text{NO}_3^-$ -N  
leaching losses ranging from 39 to  $162 \text{ kg N ha}^{-1} \text{ y}^{-1}$ .

In intensively grazed sheep, beef and dairy pasture systems, the main source of  $\text{NO}_3^-$ -N  
leached comes from the nitrogen (N) returned in the urine from grazing animals. The N  
25 loading rate under a cow urine patch is equivalent to  $1000 \text{ kg N ha}^{-1}$  and  $500 \text{ kg N ha}^{-1}$  for

sheep urine patches. This amount of N is in excess of that which can be taken up by the pasture in a growing season. The surplus N, when converted to  $\text{NO}_3^-$ , is thus prone to leaching when there is drainage through the soil profile.

- 5 The New Zealand Ministry of Health has established drinking water guidelines that limit  $\text{NO}_3^-$ -N concentration in drinking water to  $11.3 \text{ mg N L}^{-1}$ . These practices are similar to regulatory or mitigating measures taken by other countries.

- 10 Nitrate leaching from soil also increases leaching losses of potassium ( $\text{K}^+$ ), calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ), due to the need for a positively charged 'counter ion' to balance the negatively charged nitrate ( $\text{NO}_3^-$ ) ion that is leached. This represents a loss of valuable nutrients that a farmer has to replace in the form of fertilizers.

- 15 One of the management measures that has the potential to reduce  $\text{NO}_3^-$ , K, Ca and Mg leaching and nitrous oxide emissions from agricultural land is the use of nitrification inhibitors which slow down the conversion of ammonium ( $\text{NH}_4^+$ ) to  $\text{NO}_3^-$  in the soil.

- 20 Most soils in temperate regions of the world have a net negative charge, therefore  $\text{NH}_4^+$ -N is adsorbed onto the soil exchange surfaces, giving a greater opportunity for it to be taken up by plants, immobilized into soil organic matter, or fixed into certain clay mineral interlayers, rather than being leached.

- 25 Nitrous oxide ( $\text{N}_2\text{O}$ ) is both a greenhouse gas, contributing to global warming, and a gas that can cause depletion of the stratospheric ozone layer. The global warming potential of  $\text{N}_2\text{O}$  in the long-term is about 320 times that of carbon dioxide ( $\text{CO}_2$ ). The amount of  $\text{N}_2\text{O}$

directly emitted from agricultural fields may account for 20-30% of the total N<sub>2</sub>O emitted annually from the earth's surface.

In grazed grassland pasture systems, a major source of N<sub>2</sub>O emissions is the N returned  
5 in animal excreta, particularly in the urine. For example, in New Zealand N<sub>2</sub>O emissions from animal excreta account for about 50% of the country's total N<sub>2</sub>O emissions. Total N<sub>2</sub>O emissions make up about 20% of New Zealand's total greenhouse gas emissions inventory.

10 A significant reduction of N<sub>2</sub>O emissions from animal excreta in grazed pastures will therefore make a significant contribution to reducing total greenhouse gas emissions in New Zealand.

Pasture production under urine patches is higher than surrounding areas because of the N  
15 added to the soil by the urine although the efficiency of utilisation is not high.

The applicants enquiries show that nitrification inhibitors have not been used previously to treat the whole area of grazed pasture soils to: (1) reduce nitrate leaching; (2) reduce  
nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4)  
20 increase pasture production in grazed pasture systems, including both urine patch and non-urine patch areas.

A paper by Cookson, WR. and Cornforth, IS. published in October 2002 ('Dicyandiamide  
25 slows nitrification in dairy cattle urine patches: effects on soil solution composition, soil pH and pasture yield'. *Soil Biology & Biochemistry* 34, 1461-1465) simply showed that DCD

slowed down the nitrification rate in the soil, as measured in the field. The study did not provide direct evidence to show that the difference in nitrate concentration at the different soil depths was due to leaching. Other processes, e.g. immobilization, plant uptake and denitrification may have caused that difference. The study found no significant response in  
5 pasture yield or N uptake to DCD application, which is in contrast to the applicants' findings of increased pasture yield and N uptake, both in the urine and non-urine patch areas. No measurements were made or results reported for nitrous oxide emissions, or potassium, calcium or magnesium leaching losses. As will be seen below, the invention is very different to the work by Cookson and Cornforth because their work does not involve  
10 treating the total area of soil with a nitrification inhibitor (DCD) to successfully: (1) reduce nitrate leaching; (2) reduce nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in grazed pasture systems, including both the urine patch and non-urine patch areas.

15 A paper by Williamson, JC. *et al.* in 1998 ('Reducing nitrogen leaching from dairy farm effluent-irrigated pasture using dicyandiamide'. *Agriculture Ecosystems & Environment* 69, 81-88) describes the effect of adding a nitrification inhibitor (DCD) to dairy farm effluent prior to application onto the soil. The authors concluded that: "The reduction in N leached achieved by applying DCD was not sufficient to avert high N losses and environmental  
20 damage in the case of repeated, high effluent-N loadings during winter". The invention is very different to their work because their work involves treating dairy farm effluent rather than treating the whole area of grazed pasture soil with a nitrification inhibitor to successfully: (1) reduce nitrate leaching; (2) reduce nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in  
25 grazed pasture systems, including both the urine patch and non-urine patch areas.

- A paper by Thomson, RB. in 1989 ('Denitrification in slurry-treated soil...'. *Soil Biology and Biochemistry* 21, 875-882) describes the effect of adding nitrification inhibitors to dairy cattle slurry prior to injection into the soil. The invention is very different to their work because their work involves treating cattle slurry rather than treating the whole area of  
5 grazed pasture soil with a nitrification inhibitor to successfully: (1) reduce nitrate leaching; (2) reduce nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in grazed pasture systems, including both the urine patch and non-urine patch areas.
- 10 A paper by Akai-N; Ishibashi-E; Oya-M; Moritsugu-S. in 2001 ('Effects of nitrification inhibitors added to cow's urine on environmental burdens from grassland'. *Japanese-Journal-of-Soil-Science-and-Plant-Nutrition*. 72: 2, 206-213) describes the effect of mixing the DCD with the cow urine before application to a pasture soil. The invention is very different to the Japanese work because their work involves treating animal urine rather  
15 than treating the whole area of grazed pasture soil with a nitrification inhibitor to successfully: (1) reduce nitrate leaching; (2) reduce nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in grazed pasture systems, including both the urine patch and non-urine patch areas.
- 20 A paper by Wozniak *et al.* in 1999 ('Nitrification inhibitors for economically efficient and environmentally friendly nitrogen fertilization'. IFA Agricultural Conference on Managing Plant Nutrition. 29 June 1999. Barcelona, Spain) reviews the use of nitrification inhibitors to manage nitrogen supply from fertilizers. The invention is different to their work because their work involves treating fertilisers rather than treating the whole area of grazed pasture  
25 soil with a nitrification inhibitor to successfully: (1) reduce nitrate leaching; (2) reduce

nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in grazed pasture systems, including both the urine patch and non-urine patch areas.

- 5 A patent specification by Young *et al.* 1994 (US Patent 5332580) 'Fumigation method employing an aqueous solution comprising a hexametaphosphate, a thiocarbonate, and a sulfide' describes soil fumigation techniques and benefits and is therefore not directly relevant to the invention because the invention is not concerned with fumigation of soil.
- 10 A website page by Landcare Research in 2003 ('Reducing nitrous oxide flux from animal wastes'. <http://www.landcareresearch.co.nz/research/greenhouse/climate...>) describes the effect of adding a nitrification inhibitor (DCD) to dairy cattle effluent to reduce nitrous oxide emissions following land application of the mixture. The invention is very different to the Landcare Research work because their work involves treating animal effluent rather than
- 15 treating the whole area of grazed pasture soil with a nitrification inhibitor to successfully: (1) reduce nitrate leaching; (2) reduce nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in grazed pasture systems, including both the urine patch and non-urine patch areas.
- 20 A web page published by FRST in 1995 'Global effect of nitrogen' <http://www.frst.govt.nz/publications/foundation/20/9.cfm> describes the possible use of nitrification inhibitors applied with dairy shed effluent or other wastes, such as piggery wastes. The invention is very different to the work (by Landcare Research) because their work involves treating dairy shed effluent rather than treating the whole area of grazed
- 25 pasture soil with a nitrification inhibitor to successfully: (1) reduce nitrate leaching; (2)

reduce nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in grazed pasture systems, including both the urine patch and non-urine patch areas.

- 5 DCD has also been used in cropping systems (in conjunction with fertilizers) but this is not relevant because our invention refers to treating the whole area of grazed pasture soil with a nitrification inhibitor to successfully: (1) reduce nitrate leaching; (2) reduce nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in grazed pasture systems, including both the urine patch and non-urine patch areas.
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It is an object of this invention to address the foregoing problems and to provide a useful alternative choice.

- 15 Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

#### **Statements of invention**

- The invention in a first aspect provides for a soil management tool when used in pasture farming systems including the application of nitrification inhibitors in solution form and/or fine particle suspension form and/or in crystalline form to treat the whole area of grazed pasture soils as a very effective management tool to: (1) reduce  $\text{NO}_3^-$ -N leaching; (2) reduce nitrous oxide emissions; (3) reduce potassium, calcium and magnesium leaching; and (4) increase pasture production in both the animal urine patch areas and non-urine patch areas.
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The nitrification inhibitor can be applied in conjunction with irrigation water, by a vehicle or in a similar way to the application of agricultural chemicals.

5 The invention provides in another aspect a delivery mechanism for applying a nitrification inhibitor in solution form and/or fine particle suspension form and/or crystalline form to the whole area of the soil in a grazed pasture system.

The invention provides in a preferred aspect a solution and/or fine particle suspension of nitrification inhibitor when applied at a frequency and timing to a grazed pasture to reduce  
10  $\text{NO}_3^-$ -N leaching by 76% for urine-N applied in the autumn, and by 42% for urine-N applied in the spring, giving an annual average reduction of 59%, which is equivalent to reducing the  $\text{NO}_3^-$ -N leaching loss in a grazed pasture from 118 to 46 kg N ha<sup>-1</sup> y<sup>-1</sup> (Table 1 below).

15 An alternative means of delivering the inhibitor can be in a crystalline form, either on its own or in combination with other products, which allows for rainfall or irrigation to dissolve it into soil.

The invention also reduces nitrous oxide emissions (Table 3 and Figure 4); reduces potassium, calcium and magnesium leaching losses (Table 4); and increases pasture  
20 production (Figure 2 and Table 2).

Two of the most commonly used nitrification inhibitors are dicyandiamide (DCD) and nitrotyrin. DCD has several advantages, which make it a desirable choice over others. It is cheaper to produce; it is water soluble and can be applied in solution form and/or fine particle suspension form; and importantly, it decomposes completely in the soil into  $\text{NH}_4^+$



and CO<sub>2</sub>. The applicants postulate that as an alternative other nitrification inhibitors can be used, such as 3,4-dimethylpyrazole phosphate (DMPP).

- DCD can be regarded as a slow release N fertilizer (containing about 65% N), however  
5 this is not the purpose in the present invention of the proposed soil application. DCD inhibits the first stage of nitrification in soil, i.e., the oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup>, by rendering the bacteria's enzymes ineffective. It is not a bactericide, and does not affect other heterotrophs that are responsible for much of the soil's biological activity.
- 10 The purpose of this invention is to treat the whole area of grazed pasture soil, including urine patch and non-urine patch areas, to reduce the nutrient losses from the animal urine and soil, rather than from the fertilizer *per se*, and also to increase pasture production from both the urine patch and non-urine patch areas in grazed pasture systems.
- 15 The effective performance of DCD in reducing NO<sub>3</sub><sup>-</sup>-N leaching and nitrous oxide emissions from urine patches compared to the performance reported from other studies, where DCD was either applied alone or combined with N fertilizers in cropping systems or applied with manure or dairy effluent, is related to the manner in which DCD is applied. When DCD is applied in solution form and/or fine particle suspension form it is highly  
20 effective at reducing the leaching of nitrate, K, Ca, Mg, reducing nitrous oxide emissions and increasing pasture production.

- The application in solution form and/or fine particle suspension form helps the inhibitor to permeate throughout the soil surface layer enabling it to treat a greater soil volume,  
25 slowing down its decomposition compared to situations where it remains on the soil

surface following application in a solid form with N fertilizer. Multiple applications maintain the inhibition effect in the soil for a longer time period compared to a single application. Most other studies have either combined DCD with an N fertilizer applied in a solid form or mixed with a liquid manure or effluent in a single application.

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One of the keys to using nitrification inhibitors to reduce the leaching of  $\text{NO}_3^-$ , K, Ca, and Mg and reduce nitrous oxide emissions from grazed pasture soils is the delivery of the inhibitor over the entire soil surface, including the urine patches. This is achieved by applying DCD to the whole area of the grazed pasture soil in liquid form and/or fine particle suspension form for example through the irrigation system, as described in the example method below.

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Where farms are not irrigated, then the inhibitor can be applied by a spray vehicle in a similar way as agricultural chemicals (e.g. herbicides) are applied.

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Further aspects of the invention will become apparent from the following descriptions which are given by way of example.

#### Description of the Drawings and Tables

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Figure 1. Shows total annual  $\text{NO}_3^-$ -N leached from the treatments as measured on lysimeters, with and without a nitrification inhibitor (DCD).

Figure 2. Shows pasture yield as affected by the treatments measured on the lysimeters, with and without a nitrification inhibitor (DCD).

Figure 3. Shows pasture N off-take as affected by the treatments measured on the

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lysimeters, with and without a nitrification inhibitor (DCD).

Figure 4. Shows nitrous oxide emissions from animal urine patches as affected by the treatments measured on the lysimeters, with and without a nitrification inhibitor (DCD).

Figure 5. Shows a nitrification inhibitor applied through a centre pivot irrigation system.

5 Figure 6. Shows a nitrification inhibitor applied through a travelling irrigator.

Figure 7. Shows the active soil zone of the inhibitor, with and without irrigation.

Figure 8. Shows a pumping system for delivery of a nitrification inhibitor through an irrigation system.

10 Figure 9. Shows a nitrification inhibitor being delivered by an agricultural spray vehicle.

Table 1. Shows calculated paddock-averaged annual  $\text{NO}_3^-$ -N leaching losses and concentrations in the drainage water, with and without a nitrification inhibitor (DCD).

Table 2. Shows annual average pasture yield in urine patch and non-urine patch areas with and without a nitrification inhibitor (DCD) applied at  $15 \text{ kg ha}^{-1} \text{ y}^{-1}$  to field plots on a

15 Temuka soil type.

Table 3. Shows nitrous oxide emissions, with and without a nitrification inhibitor (DCD).

Table 4. Shows calculated paddock-averaged potassium, calcium and magnesium leaching losses, with and without a nitrification inhibitor (DCD).

## 20 **Modes for carrying out the invention**

Modes of carrying out the invention will become apparent from the following descriptions

which are given by way of example only.

### Example 1

5 Lysimeter studies, which are state-of-the-art technology for these investigations, have shown the effectiveness of a nitrification inhibitor, dicyandiamide (DCD), in reducing  $\text{NO}_3^-$ -N leaching from a grazed dairy pasture under irrigation. This example used a free-draining Lismore stony silt loam (Udic Haplustept loamy skeletal) and the pasture was a mixture of perennial ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*) but the process is  
10 applicable to all temperate soils and animal grazing systems.

Undisturbed soil monolith lysimeters, 50 cm diameter and 70 cm deep, were collected following well-established protocols and procedures that ensure there is minimal disturbance to the soil structure inside. The lysimeters were transported to a lysimeter  
15 facility near Lincoln University, using a specially designed trailer with air-bag suspension to minimize disturbance. The gap between the soil core and the metal casing was sealed using petroleum jelly to stop edge-flow effects. The lysimeters were then installed in the field lysimeter facility with the surface of the lysimeters at the same level as that of the surrounding soil surface, in order to maintain normal plant growing conditions.

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Each treatment had 4 replicates. The treatments were allocated to the lysimeters in a randomised design. The urea application rate of  $200 \text{ kg N ha}^{-1} \text{ y}^{-1}$  was at the higher end of fertilizer N application rates for most farmers in the region. The rates of urea were either split into 8 applications to maximize N efficiency, or 4 applications as a cost cutting  
25 measure (i.e. reducing application costs). Urine was applied either in the spring (November) or in the autumn (April) to simulate urine patches deposited in the spring or

autumn by a grazing dairy cow. The urine application rate of  $1000 \text{ kg N ha}^{-1}$  was equivalent to the typical N loading rate under a cow urine patch. The combination of urea with urine treatments was included to represent a situation where urea was applied throughout the paddock, and patches of the paddock received cow urine. Two rates of phosphate (P) fertilizer were applied, 45 or  $90 \text{ kg P ha}^{-1} \text{ y}^{-1}$ , to represent the range of P application rates used by local dairy farmers. As the purpose of this study was to determine the effectiveness of DCD in reducing  $\text{NO}_3^-$  leaching from grazed pasture soil including cow urine patch areas, DCD was either applied or withheld. The DCD was applied in a liquid form to simulate application in the irrigation water on irrigated dairy farms or by spray vehicle.

Urea was applied in solid form and was broadcast over the surface of the lysimeters followed by 10 mm of irrigation. Irrigation following urea application has been shown to significantly reduce ammonia loss by volatilization.

Fresh urine was collected early in the morning during the milking session from Friesian cows, and was analysed and applied to the lysimeters on the same day. The same volume of water was applied to the other lysimeters that did not receive urine in order to maintain the same moisture input to all lysimeters.

DCD was applied in solution form (100 mL per lysimeter) at the rates of  $7.5 \text{ kg ha}^{-1}$  after each urea application in the same day, or  $15 \text{ kg ha}^{-1}$  immediately after each urine application. The DCD solution was sprayed onto the lysimeters with a watering can, simulating an application by an irrigator or spray vehicle.

From November to April (late spring to mid autumn), flood irrigation, at 100 mm, was applied to all the lysimeters at about three weekly intervals. The amount of water applied was to represent the average amount of water applied on commercial flood-irrigated dairy farms. Irrigation water was applied using an electronically controlled metering system to deliver the required volume of water to the lysimeters. From May to October (late autumn to mid spring), simulated rainfall was applied at the end of each month (if necessary), to supplement the natural rainfall received in order to equal the 75th percentile of local rainfall records for the same period of the year. This was done to create a so-called 'worst case scenario' in terms of rainfall inputs and to ensure a standard condition was achieved.

The herbage was cut periodically to simulate typical grazing practice. All the harvested herbage was removed and dry matter yield recorded. Herbage nitrogen content was analysed. Following each herbage cut, a specially designed mechanical cow hoof was used to simulate cow treading on the lysimeters. The mechanical hoof is made of stainless steel with identical shape and size as an adult Friesian cow hoof. The hoof is mounted onto a compressed air-ram, which is driven by an air compressor system to provide a treading pressure of 220 kPa to simulate the treading pressure exerted by a cow's hoof during walking. The entire surface of the lysimeters was trodden once following each herbage cut. This was based on the inventors observation of hoof print coverage following each grazing rotation.

Nitrous oxide emissions from two treatments were determined using a closed chamber method. The enclosed chamber was fitted on top of the lysimeters inside a rubber ring on top of the lysimeter casing. At each sampling time, 3 samples, 10–15 minutes apart, were

taken. Nitrous oxide was analysed using gas chromatography and daily N<sub>2</sub>O fluxes were calculated based on daily mean temperatures.

A field plot experiment was established on a Temuka soil on the Lincoln University Dairy farm to determine pasture response to DCD applications. A total of six plots, each 100 m<sup>2</sup> in area were set up. Fresh cow urine was collected from dairy cows and was analysed for N concentration. The urine was then applied to eight areas (0.2 m<sup>2</sup> each) within each plot to simulate urine patches deposited by the grazing cow. Urea was applied to the plots as per the rest of the farm at 200 kg N/ha. Phosphate fertilizer (superphosphate) was applied at 45 kg P/ha per year as per the rest of the dairy farm.

Three of the plots received the DCD treatment. DCD was applied in a solution form to the whole area of each plot by spray equipment similar to those used to spray other agrochemicals. The DCD was applied twice each year (one in the autumn (May) and one in the spring (August)) at 10-15 kg/ha for each application.

Spray irrigation was applied between spring and autumn when necessary through a central pivot irrigator as per the rest of the dairy farm. Pasture from the simulated urine patch areas and from adjacent non-urine patch areas was cut and removed. Following the pasture cut, the plots were then grazed by dairy cows.

Dry matter yield was recorded from the urine patch and non-urine patch areas (Table 2). Pasture yield was calculated at the paddock scale as described above (Table 2).

Table 1. Calculated paddock-averaged annual  $\text{NO}_3^-$ -N leaching losses and concentrations in the drainage water, with and without a nitrification inhibitor (DCD).

Management condition	Leaching losses from paddock <sup>c</sup> (kg N ha <sup>-1</sup> y <sup>-1</sup> )	Paddock averaged concentration (mg N L <sup>-1</sup> )
Urea 200 + grazing <sup>a</sup>	118.2	19.7
Urea 200 + grazing + DCD <sup>b</sup>	46.1	7.7

<sup>a</sup>Assuming that urea was applied at 200 kg N ha<sup>-1</sup> y<sup>-1</sup> throughout the paddock, and urine patches covered 25% of the paddock (equivalent to 3 cows per ha.).

<sup>b</sup>As above except with DCD applied, as described in the text.

<sup>c</sup>To calculate these values, annual leaching losses from urine areas were the averages of those from the urine applied in the spring and autumn. The autumn leaching losses were the averages of the P45 and P90 treatments. The leaching losses from the urea 200 treatment with DCD were assumed to be 59.1% less than that from the urea 200 treatment without DCD.

Table 2. Annual average pasture yield in urine patch and non-urine patch areas with and without a nitrification inhibitor (DCD) applied at 15 kg ha<sup>-1</sup> y<sup>-1</sup> to field plots on a Temuka soil type.

Management condition	Pasture yield (t ha <sup>-1</sup> y <sup>-1</sup> )
<b>No DCD applied</b>	
Urine patch areas	13.4
Non-urine patch areas	10.3
<b>With DCD applied</b>	
Urine patch areas	15.1
Non-urine patch areas	12.3
<b>Paddock averaged yields</b>	
No DCD <sup>a</sup>	11.1
With DCD applied <sup>b</sup>	13.0

<sup>a, b</sup>Similar assumptions were made as those for calculating  $\text{NO}_3^-$ -N leaching losses in Table 1.



Table 3. Shows nitrous oxide emissions, with and without a nitrification inhibitor (DCD) applied. (Numbers in brackets are standard error of the mean.)

Treatment	Total nitrous oxide emission (kg N <sub>2</sub> O/ha)
Autumn application	
Urine (no DCD )	26.7 (5.9)
Urine + DCD	7.0 (2.3)
Spring application	
Urine (no DCD)	18.0 (2.9)
Urine + DCD	4.5 (0.7)

Table 4. Shows calculated paddock-averaged potassium, calcium and magnesium leaching losses, with and without a nitrification inhibitor, assuming 25% of the area is covered by urine patches.

Cation	Leaching losses (kg ha <sup>-1</sup> y <sup>-1</sup> )		
	Without DCD	With DCD	% decrease due to DCD
Calcium (Ca <sup>2+</sup> )	213	107	50%
Potassium (K <sup>+</sup> )	48	17	65%
Magnesium (Mg <sup>2+</sup> )	17	8	52%

## Example 2

### Delivery Systems for applying a Nitrification Inhibitor through an Irrigation System

5 The intent is to spread the nitrification inhibitor evenly over the whole surface of the pasture soil by applying it through an irrigation system (such as centre pivot or travelling irrigator) where there is an ability to control and vary the application volume and rate of application according to the conditions in the soil (an example applicator is illustrated in  
10 Figs 5 and 6).

Delivery of the inhibitor in solution and mixed with the irrigation water ensures that the inhibitor penetrates throughout the soil surface. The ability to control the penetration of the inhibitor through the soil volume is a key determinant of the effectiveness of the  
15 compound. The effectiveness of the inhibitor is increased by distribution throughout, and thus treats, a larger volume of soil (Fig. 7) than it would if the inhibitor alone was sprayed onto the pasture soil surface. This is an advantage of such a delivery system where the soil moisture content varies from wilting point to field capacity throughout the year and in turn affects the flow of the applied solution.

20 A computer controlled pumping system can be part of the inhibitor delivery system. The nitrification inhibitor solution at a concentration dependent on the level of control required over the processes in the soil is injected from a supply tank into the irrigation water using a flow rate controlled pump connected to the irrigation delivery pipe or irrigation hose (as  
25 illustrated in Fig. 8).

The timing of application is important to the success of the process. The irrigator and pumping systems are controlled such that the nitrification inhibitor is applied to the paddock soon after grazing, when the urine patches are fresh, by following the grazing  
30 rotation. This is particularly important for the autumn grazing rotations.

### Example 3

#### Delivery of a nitrification inhibitor using agricultural chemical spray equipment

- 5 The nitrification inhibitor can be delivered evenly over the soil surface using agricultural chemical spray equipment (e.g., equipment currently used to apply agricultural chemicals such as herbicides or pesticides).

10 The nitrification inhibitor is delivered/dissolved in water and the solution and/or fine particle suspension is sprayed onto the whole surface of the grazed pasture soil from a tank of an agricultural spray vehicle.

The spray equipment can be used to apply the nitrification inhibitor immediately after grazing when the animal urine patches are 'fresh', this can be particularly effective during  
15 autumn grazing rotations.

Following the spray application by this method irrigation water can be applied to 'wash' the nitrification inhibitor into the topsoil. This will ensure that the nitrification inhibitor is distributed evenly throughout, and thus treats, the topsoil.

20 If irrigation is not applied then the nitrification inhibitor can be applied immediately prior to rainfall. The rain will 'wash' the inhibitor into the topsoil and thus ensure that this larger volume of soil is treated.

#### 25 Advantages

The invention provides a number of advantages some of which are listed below.

- 30 1. The  $\text{NO}_3^-$ -N concentration in the drainage water from a grazed dairy pasture soil is reduced accordingly from 19.7 to 7.7 mg N L<sup>-1</sup>, with the latter being below the World Health Organisation and New Zealand Ministry of Health drinking water guideline of 11.3 mg N L<sup>-1</sup> (Table 1).

2. A solution of nitrification inhibitor (DCD) when applied at a frequency and timing to a grazed dairy pasture increases pasture production from the whole of the grazed pasture by more than 15% (e.g, from 11.1 to 13.0 t ha<sup>-1</sup> y<sup>-1</sup>) (Table 2).

3. Total annual NO<sub>3</sub><sup>-</sup>-N leaching losses measured from the lysimeters were low in the Control (4.8 kg N ha<sup>-1</sup> y<sup>-1</sup>) and in the Urea 200 treatment (Treatment 2: 7.9 kg N ha<sup>-1</sup> y<sup>-1</sup>) (Figure 1). In Treatment 3 where urine was applied in the autumn without DCD, total NO<sub>3</sub><sup>-</sup>-N leaching loss was equivalent to 516 kg N ha<sup>-1</sup> y<sup>-1</sup> (i.e. directly below the urine patch). This was reduced to 128 kg N ha<sup>-1</sup> y<sup>-1</sup> when DCD was applied (Treatment 4) (Figure 1).

4. Similarly, in the P 90 treatments (cf. Treatments 5 and 6), the application of DCD reduced total annual NO<sub>3</sub><sup>-</sup>-N leaching loss from 488 to 112 kg N ha<sup>-1</sup> y<sup>-1</sup>. Where the urine was applied in the spring (cf. Treatments 7 and 8), the application of DCD reduced total annual NO<sub>3</sub><sup>-</sup>-N leaching loss from 397 to 230 kg N ha<sup>-1</sup> y<sup>-1</sup> (Figure 1). These results show that the application of DCD reduced NO<sub>3</sub><sup>-</sup>-N leaching by an average of 76.1% for the urine-N applied in the autumn, and by 42.1% for the urine N applied in the spring.

5. When urea was applied at 200 kg N ha<sup>-1</sup> y<sup>-1</sup> throughout the paddock and the paddock was grazed by 3 cows per ha, the average annual NO<sub>3</sub><sup>-</sup>-N leaching loss from the whole paddock was estimated to be 118 kg N ha<sup>-1</sup> y<sup>-1</sup> without DCD. This was reduced to 46 kg N ha<sup>-1</sup> y<sup>-1</sup> (Table 1) when DCD was applied to the whole area of the grazed pasture soil. The application of DCD would reduce the NO<sub>3</sub><sup>-</sup>-N concentration in the drainage water from 19.7 to 7.7 mg N L<sup>-1</sup>. The latter was below the drinking water guideline of 11.3 mg N L<sup>-1</sup> set by the New Zealand Ministry of Health. Most of the NO<sub>3</sub><sup>-</sup>-N leached was contributed by that leached from the urine patch areas (Table 1).

6. The application of DCD increases pasture yields (Figure 2). The increases in pasture yields were particularly evident in the autumn urine treatments (cf. Treatments 3 and 4; and 5 and 6 in Figure 2). The application of DCD increased pasture yields in the autumn urine treatments by an average of 49%, while the increase in the spring urine treatments was equivalent to 17.5%. This gave an annual average increase of more than 15% in pasture production by treating the whole surface area with DCD. The pasture yields were higher in the spring urine treatments than in the autumn urine treatments.

7. The increases in pasture N off-take as a result of DCD application were equivalent to 23% for the autumn urine treatments, and 9% for the spring urine treatments, giving an annual average of 16% (Figure 3).

5 8. Pasture yields were also found to increase in large field plots treated with DCD. This trial showed that the annual pasture yield in the urine patch areas increased from 13.4 to 15.1 t ha<sup>-1</sup> y<sup>-1</sup> when DCD was applied to the whole area of the grazed pasture soil in the field plots (Table 2). Pasture yield was also increased in the non-urine patch areas from 10.3 to 12.3 t ha<sup>-1</sup> y<sup>-1</sup> when DCD was applied to the whole area of the grazed pasture  
10 soil in the field plots (Table 2). The calculated average paddock yield increased from 11.1 to 13.0 t ha<sup>-1</sup> y<sup>-1</sup> when DCD was applied to the whole area of the grazed pasture soil in the field plots (Table 2).

9. The application of DCD applied in solution or fine particle suspension forms to the  
15 whole area of grazed pasture soil appears to be a very effective management tool to reduce NO<sub>3</sub><sup>-</sup>-N leaching in a grazed pasture system. The use of DCD alone could reduce NO<sub>3</sub><sup>-</sup>-N concentration in the drainage water from 19.7 to 7.7 mg N L<sup>-1</sup> in a shallow and stoney free-draining Lismore soil which is a soil that has a very high leaching potential. Therefore, with the use of DCD, the NO<sub>3</sub><sup>-</sup>-N concentration in the drainage water from free-  
20 draining soils can be reduced significantly below the drinking water guideline of 11.3 mg N L<sup>-1</sup>.

10. For instance, combined DCD with farm dairy effluent (dirty water) reported only an 18% reduction in the amount of NO<sub>3</sub><sup>-</sup>-N leached. This was significantly lower than the  
25 42.1-76.1% reductions in the amount of urine N leached as measured in this study.

11. The rate of DCD decomposition increases with temperature. This is probably one of the reasons why the reduction in NO<sub>3</sub><sup>-</sup> leaching from the spring urine application was smaller than that from the autumn urine application, as the DCD would have been  
30 decomposed more rapidly under the warmer summer temperatures. However, the fact that DCD was only applied 5 times in the spring urine treatment compared to 9 applications in the autumn urine treatments might also have played a part in contributing to

the differences in the DCD effect. In line with findings in a previous study using the same soil the amount of  $\text{NO}_3^-$ -N leached from the spring urine without DCD was lower than that from the autumn urine partly due to greater pasture N off-take of the spring urine N (Figure 3). The optimum frequency and amount of DCD application are the subject of the inventors' current investigations. Indications are that it may be possible to use two applications per year (e.g. spring and autumn) to achieve similar results as described above.

12. The use of DCD increases pasture production (Figure 2, Table 2). The slow down of nitrification therefore preserves the N in the  $\text{NH}_4^+$  form for a longer period, making it more accessible for pasture uptake. This increase in pasture production in both the urine patch and non-urine patch areas (Table 2) is an added benefit from applying DCD onto the whole area of grazed pasture soils. The additional amount of N applied from the DCD was small ( $20\text{--}49\text{ kg N ha}^{-1}\text{ y}^{-1}$ ), particularly compared with the  $1000\text{ kg ha}^{-1}$  of urine N applied, the effect on pasture production by the DCD-N alone was, therefore, probably limited.

13. The amount of  $\text{NO}_3^-$ -N leached from the Urea 200 treatment ( $8\text{ kg N ha}^{-1}\text{ y}^{-1}$ , Treatment 2, Figure 1) was slightly lower than that ( $17\text{ kg N ha}^{-1}\text{ y}^{-1}$ ) from a previous study using the same soil. This difference in leaching loss was probably because the 200 kg of urea N in this study was split into 8 applications whereas in the previous study, it was split into 4 applications. The practice of more frequent applications of smaller amounts of N was thus probably slightly more efficient than that of fewer applications at greater amounts.

14. By treating the whole area of grazed pasture soil with DCD, including the urine and non-urine patch areas, the amount of  $\text{NO}_3^-$  leaching can be dramatically reduced. The use of DCD reduced  $\text{NO}_3^-$ -N leaching by 76% for the urine N applied in the autumn, and by 42% for urine N applied in the spring, giving an annual average reduction of 59%. This was found to reduce the  $\text{NO}_3^-$ -N leaching loss in the whole area of a grazed paddock from 118 to  $46\text{ kg N ha}^{-1}\text{ y}^{-1}$ .

15. The  $\text{NO}_3^-$ -N concentration in the drainage water was reduced accordingly from 19.7 to 7.7 mg N L<sup>-1</sup>, with the latter being below the drinking water guideline of 11.3 mg N L<sup>-1</sup>. In addition to the environmental benefits, the use of DCD also increased pasture production by more than 15%, from 11.4 to 15.0 t ha<sup>-1</sup> y<sup>-1</sup>.

16. Nitrous oxide ( $\text{N}_2\text{O}$ ) emissions following urine application in autumn were reduced from 26.7 kg  $\text{N}_2\text{O}$ -N ha<sup>-1</sup> without DCD to 7.0 kg  $\text{N}_2\text{O}$ -N with DCD (Table 3 and Figure 4); and following a spring application were reduced from 18.0 kg  $\text{N}_2\text{O}$ -N ha<sup>-1</sup> without DCD to 4.5 kg  $\text{N}_2\text{O}$ -N ha<sup>-1</sup> with DCD applied (Table 3).

17. These results suggest that the effective use of DCD has the potential to transform grazed pasture systems to a more environmentally sustainable basis by reducing  $\text{NO}_3^-$ , K, Ca and Mg leaching and  $\text{N}_2\text{O}$ -N losses.

18. The application of a nitrification inhibitor (e.g. DCD) reduced calcium ( $\text{Ca}^{2+}$ ) leaching by 50% (from 213 to 107 kg/ha/y), reduced potassium ( $\text{K}^+$ ) leaching by 65% (from 48 to 17 kg/ha/y) reduced magnesium ( $\text{Mg}^{2+}$ ) leaching by 52% (from 17 to 8 kg/ha/y) (Table 4). This would provide economic benefit to the farmer in reduced fertilizer costs.

19. The delivery system for applying an active nitrification inhibitor through an irrigation system can produce the effects described above.

20. The delivery system for applying an active nitrification inhibitor using agricultural chemical spray equipment can produce the effects as described above.

In Figure 5 is shown a centre pivot irrigation system 1 suitable for application of a nitrification inhibitor in solution or fine particle suspension form. The supply of the nitrification inhibitor to the irrigation water can be from reservoir 2 by way of a venturi pipe or pump. The irrigation water being supplied from an underground water supply 3 or irrigation supply system.

In Figure 6 is shown a travelling irrigator 1 suitable for application of a nitrification inhibitor in solution or fine particle suspension form. The supply of the nitrification inhibitor to the

irrigation water can be from reservoir 3 by way of a venturi pipe or pump. The irrigation water is supplied from an underground water supply 2 or irrigation system.

In Figure 8 is shown a delivery system suitable for delivering at a controlled rate a  
5 nitrification inhibitor to an irrigation system. The irrigation water plus nitrification inhibitor 1 is delivered at a controlled rate to an irrigator (not shown). The rate of nitrification inhibitor supply is controlled by a control system 2 which monitors a flow rate sensor 3. The control system 2 monitors and controls the supply of nitrification inhibitor from reservoir 6 through injection pump 5 to a control valve 4. The control system 2 operates in conjunction with an  
10 irrigation pump 7 to supply the irrigation water for the irrigator.

In Figure 9 is shown diagrammatically the application of a nitrification inhibitor delivered by an agricultural spray vehicle. The vehicle has a tank 1 containing a nitrification inhibitor solution or fine particle suspension and a spray boom 2 for applying inhibitor over the soil  
15 surface.

Where in the description and examples particular integers are mentioned it is envisaged that their equivalents may be substituted as if they were individually set forth herein.

20 Particular examples of the invention have been described and it is envisaged that improvements and modifications can take place without departing from the scope of the attached claims.